Heterogeneous photocatalytic treatment of pharmaceutical micropollutants: Effects of wastewater effluent matrix and catalyst modifications

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ABSTRACT

This study evaluates the applicability of TiO_2-based photocatalysts for the treatment of pharmaceutical micropollutants in secondary wastewater effluent (SWE). Photolytic experiments using SWEs with different compositions demonstrated that the rates of photocatalytic degradation of acetaminophen and carbamazepine inversely correlated with the concentration of dissolved organic carbon (DOC), regardless of the type of applied light source and initial pharmaceutical concentration. The critical relevance of organic matter to the scavenging behavior of SWE was further verified by assessing the photocatalytic performance as a function of the concentrations of potential effluent-derived quenchers (i.e., NO_3^-, Cl^-, alkalinity, and humic acid). Kinetic comparison of the degradation of trace levels of pharmaceuticals (i.e., caffeine, cimetidine, propranolol, and sulfamethoxazole) using TiO_2/UV-A, TiO_2/UV-C, and H_2O_2/UV-C systems revealed that heterogeneous processes showed more significant performance reduction with increasing DOC concentration; this result indicates that organic matter plays dual roles in the scavenging activity of an effluent matrix: (1) OH radical ($^{\bullet}OH$) quenching and (2) active-site coverage. TiO_2 surface modifications (i.e., Pt and SiO_x loading) accelerated the degradation of all the tested pharmaceuticals in SWEs to a certain degree. Particularly, the relevant altered surface affinity preferentially increased the susceptibility of specific pharmaceuticals to photocatalytic treatment. The presence of the effluent matrix substantially impaired the performance of visible-light-active photocatalysts in most cases. However, photocatalytic pharmaceutical degradation on Pt-doped TiO_2, which occurs via direct charge transfer, was much less hindered in SWEs than that on Pt-deposited WO_3, which occurs via $^{\bullet}OH$-mediated oxidation.

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1. Introduction

Advanced oxidation processes (AOPs), which involve the *in-situ* production of highly reactive oxygen species (e.g., hydroxyl radical ($^{\bullet}OH$)) in contaminated environmental media, constitute a promising strategy for the remediation of municipal and industrial wastewater that contains recalcitrant organic substances [1–3]. In contrast to the substrate-dependent activities of chemical oxidants (e.g., chlorine and ozone) and microbial communities used in conventional water treatment infrastructures, the indiscriminate nature of $^{\bullet}OH$-induced oxidation [4] enables the application of AOPs to the degradation and mineralization of a wide range of organic compounds. As a result, $^{\bullet}OH$ effectively mediates the chemical transformation of bio-refractory organics into intermediates that are highly vulnerable to microbial degradation, which indicates the potential suitability of AOPs as a pre-treatment for biological processes [5,6]. AOPs are also considered to be a post-treatment option for the oxidative destruction of emerging organic contaminants (e.g., endocrine disruptors, pharmaceuticals, and personal care products) that survive secondary biological treatment [7,8].

Pharmaceutical compounds are biologically active in trace quantities and conserve their behavior after being discharged into

aquatic environments, raising concerns regarding the potential risks to the environment and human health [9,10]. Treatability studies have reported significant substrate-specific variation in the removal efficacy of physicochemical and biological processes [11,12]; this implies that select groups of pharmaceuticals could pass intact through conventional water treatment facilities. On the other hand, recent performance assessments have shown that AOPs based on the non-selective reactivity of •OH rapidly degraded a broad spectrum of pharmaceuticals [1,8,13]. For instance, hydrogen peroxide (H_2O_2) in conjunction with UV light (H_2O_2/UV) is highly efficient for the treatment of most of the pharmaceutical substances (e.g., analgesics, antiarrhythmic agents, and antibiotics) that are present in secondary wastewater effluent, while UV photolysis alone degrades only a limited number of pharmaceuticals [8]. Fenton treatment of secondary effluent also leads to complete removal of various trace-level pharmaceuticals including caffeine, carbamazepine, ibuprofen, naproxen, sulfamethoxazole, and trimethoprim [14]. The combination of H_2O_2 and alkaline pH conditions, which facilitate the decomposition of ozone into •OH, kinetically enhances the ozonation of pharmaceuticals and their metabolites in biologically pre-treated municipal wastewater [15].

Titanium dioxide (TiO_2) that requires a relatively low photon energy for charge separation can photosensitize oxidative degradation of organic compounds via production of powerful oxidizing species under artificial UV and solar light irradiation [16,17]. Similar to AOPs, a multi-activity assessment using a diverse range of pharmaceuticals suggested that heterogeneous TiO_2 photocatalysis as an effective approach for the high-yield generation of •OH is applicable for the remediation of pharmaceutical-polluted water bodies [18,19]. On the other hand, most investigations into the treatability of pharmaceuticals by TiO_2 photocatalytic systems [18–22] have been conducted using relatively high concentrations of pharmaceuticals (typically ranging from 10 to 500 μM) in deionized or distilled water; this is in contrast to the applicability assessments of homogeneous AOPs (e.g., O_3/UV and H_2O_2/UV), which have been tested on trace levels of pharmaceuticals in secondary effluent matrices [18,19]. There is a high likelihood that effluent-derived inorganic ions (e.g., NH_4^+, NO_3^-, and HCO_3^-) modify the surface charge of TiO_2 and, consequently, its adsorption affinity toward organic substances. Background organic matter, which acts as a •OH sink in wastewater effluent and surface waters probably causes a competition with organic micropollutants for •OH-mediated oxidation on photoirradiated TiO_2. Therefore, characterization of the TiO_2 photocatalytic oxidation of pharmaceutical micropollutants under experimental conditions that include realistic water compositions needs to be prioritized for the rational evaluation of the activity of TiO_2-based photocatalysis as a viable tertiary treatment option.

This study demonstrates the potential application of heterogeneous TiO_2 photocatalysts for the removal of trace-level (typically 1 μM) pharmaceuticals, including acetaminophen, caffeine, carbamazepine, cimetidine, propranolol, and sulfamethoxazole, in secondary wastewater effluents (SWEs). The effect of the water quality on photocatalytic oxidation kinetics is investigated using effluents from four municipal wastewater treatment plants and distilled water suspensions containing background constituents at varying concentrations that have been spiked with pharmaceuticals. We evaluate the impact of the background water matrix on the performance of TiO_2 photocatalysts for the treatment of pharmaceuticals relative to direct UV photolysis and H_2O_2/UV. Various photocatalyst modifications, i.e., surface platinization, silica loading, and transition metal and non-metal doping, are examined in order to improve the heterogeneous photocatalytic systems by kinetically enhancing pharmaceutical oxidation and reducing the energy required for catalyst activation.

2. Materials and methods

2.1. Reagents

The chemicals that were used in this study include tungsten oxide (WO_3, nanopowder), chloroplatinic acid hydrate(H_2PtCl_6), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), titanium tetraisopropoxide (TTIP, $Ti(OCH(CH_3)_2)_4$), acetaminophen, acetic acid, phosphoric acid, and ethanol, which were purchased from Aldrich. Caffeine, carbamazepine, hydrogen peroxide solution, methanol, and perchloric acid were sourced from Sigma–Aldrich, while cimetidine and propranolol were purchased from Sigma. Titanium dioxide (TiO_2, Degussa P25), sulfamethoxazole (Fluka), acetonitrile (J.T. Baker), Ti(IV) sulfate solution (Kanto chemical), and sodium hydroxide solution (Fluka) were also used. Ultrapure deionized water (18 MΩ cm) prepared with a Millipore system was used. All chemicals were of reagent grade and used without further purification.

2.2. Photochemical experiments

Photolytic experiments using various light sources, i.e., a germicidal lamp, black light blue lamp, and fluorescent lamp (output power: 4 W; Philips Co.), were performed in a magnetically stirred 60 mL cylindrical quartz reactor at ambient temperature (22 ± 1 °C). The emission spectra of the three types of lamps were recorded using a Spectropro-500 spectrophotometer (Acton Research Co.) (Supplementary Data, Fig. S1). The UV intensities of the germicidal and black light blue lamps were 1.8 and 0.7 mW/cm^2, respectively, as measured using a UVX radiometer (Ultraviolet Products Ltd.) equipped with a UVX-25 or UVX-36 sensor. The experiments that used visible-light-active photocatalysts were performed with a UV cut-off filter, which blocks the irradiation of the UV fractions of fluorescent lamp emission (λ > 400 nm).

The photocatalytic reactions proceeded in un-buffered aqueous suspensions containing 0.5 g/L photocatalyst and the target pharmaceutical compounds (typically 1 μM) under air-equilibrated conditions. The photocatalytic oxidation of the pharmaceuticals spiked in SWEs was performed without initial pH adjustment, while the initial pH of the distilled water suspensions was tuned to around 8.0 (i.e., close to the original pH level of the secondary effluent) using 1 M $HClO_4$ or NaOH solutions. Aliquots (1 mL) were withdrawn from the photoirradiated reactor at predetermined time intervals using 1 mL syringes, filtered through 0.45 μm PTFE filters (Whatman), and injected into 2 mL amber glass vials for further analysis for target substrates. More than duplicate photolytic experiments were performed for each given condition. The residual concentrations of pharmaceutical compounds were quantitatively analyzed via high-performance liquid chromatography (HPLC) using a Shimadzu LC-20AD instrument equipped with a C-18 column (ZORBAX Eclipse XDB-C18, Agilent) and a UV/vis detector (SPD-20AV, Shimadzu). The mobile phase comprised a binary mixture of 0.1% (v/v) aqueous phosphoric acid solution and acetonitrile.

2.3. Evaluation of oxidizing capacity

Methanol and benzoic acid were used as chemical probes for detecting photogenerated •OH. The photolytic experiments were performed in aqueous suspensions of photocatalysts containing excess amounts of probe compounds (200 mM methanol and 10 mM benzoic acid) to make sure that the photoproduced •OH was completely scavenged by the chemical indicators. Formaldehyde and p-hydroxybenzoic acid as the primary oxidation products were quantitatively analyzed using the HPLC. Chemical derivatization

Table 1
Composition of the secondary effluent from four selected municipal wastewater treatment plants.

	Jungrang (JR)	Pankyo (PK)	Gwangju (GJ)	Gumi-1[a](GM-1)	Gumi-2[b](GM-2)
pH	6.6	7.8	7.8	7.2	7.3
Alkalinity (mg/L $CaCO_3$)	60.1	78.1	92.7	124.1	84.7
DOC (mg/L)	3.7	4.6	5.0	6.5	5.6
NO_2^- (mg/L)	N.D.	N.D.	5.9	N.D.	N.D.
NO_3^- (mg/L)	53.5	23.9	33.9	41.8	20.5
NH_4^+ (mg/L)	N.D.	N.D.	N.D.	N.D.	1.2
Cl^- (mg/L)	66.5	70.9	N.D.	514.6	187.8

[a] Effluent sample collected in November 2012.
[b] Effluent sample collected in March 2013.

with 2,4-dinitrophenyl hydrazine was carried out prior to the HPLC determination of formaldehyde.

2.4. Wastewater characterization

Biologically treated SWE samples were obtained from four Korean municipal wastewater treatment plants: Jungrang (JR, Seoul), Pankyo (PK, Gyeonggi-do), Gwangju (GJ, Jeollanam-do), and Gumi (GM, Gyeongsangbuk-do). The water samples were vacuum-filtered through 0.45 μm cellulose acetate membranes immediately upon receipt and stored at 4 °C prior to use in the experiments. The water quality parameters, e.g., pH, alkalinity, dissolved organic carbon (DOC), and nitrite, nitrate, ammonia, and chloride concentrations, are listed in Table 1.

2.5. Photocatalyst surface modification

Surface platinization of the photocatalysts (i.e., TiO₂ and WO₃) was performed using a photodeposition method [23]. An aqueous suspension of 0.5 g photocatalyst with 1 M methanol (electron donor) and 0.1 mM chloroplatinic acid was photoirradiated with a 200 W mercury lamp for 30 min. The platinized photocatalyst powder was separated from the suspension via membrane filtration (through a 0.45 μm membrane filter), washed with Milli-Q water, and dried at 60 °C in a thermostat oven. The typical Pt-loading on the catalyst was ca. 0.5 wt% based on quantification of the unreacted chloroplatinic acid in the filtrate solution using atomic absorption spectrometry. Transmission electron microscopy (TEM) images confirm the uniform dispersion of Pt nanoparticles on the surface of the photocatalysts (Supplementary Data, Fig. S2). Si-Modified TiO₂ (SiO$_x$/TiO₂) was prepared according to a previously reported method [17]: 30 μL Si(OC₂H₅)₄ and 0.1 g TiO₂ powder were physically mixed to achieve a uniform coating on the TiO₂ surface. The resultant powder was air-dried overnight and calcined at 500 °C for 5 h. X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, Ulvac-PHI) using an Al Kα (1486.6 eV) excitation source was used to determine the oxidation states of the Pt deposited on TiO₂ and WO₃, (Supplementary Data, Fig. S3) and surface chemical composition of SiO$_x$/TiO₂ (Supplementary Data, Fig. S4).

2.6. Photocatalyst doping

Pt-doped TiO₂ photocatalyst (Pt$_d$-TiO₂) was prepared using a sol–gel method [24]. A solution of chloroplatinic acid (as a precursor of the dopant) in ethanol (20 mL) was added to TTIP (90 mL) to obtain a Pt/Ti molar ratio of 0.005. The mixture was then added dropwise to a 0.4% (v/v) aqueous acetic acid solution (500 mL). The resultant colloidal suspension was stirred at 80 °C for 4 h and then evaporated at 50 °C using a rotary evaporator. The obtained powder was calcined in air at 450 °C for 3 h. The N-doped TiO₂ photocatalyst (N$_d$-TiO₂) was prepared by thermal treatment of Degussa P25 TiO₂ in a tube furnace at 600 °C for 4 h under an NH₃ atmosphere

[25]. The crystalline phases of the synthesized doped TiO₂ catalysts (i.e., Pt$_d$-TiO₂ and N$_d$-TiO₂) were identified using an X-ray diffractometer (Rigaku D/MAX-2500, 18 kV) with Cu Kα₁ radiation. The extended absorption in the visible light region was confirmed using a UV–vis spectrophotometer (Varian Cary 100) equipped with a diffuse reflectance accessory. The X-ray diffraction (XRD) patterns indicate that Pt$_d$-TiO₂ consisted of only the anatase phase, while the N$_d$-TiO₂ phase was primarily anatase phase with a small portion of rutile phase (Supplementary Data, Fig. S5). The diffuse reflectance spectra of doped TiO₂ demonstrate that the introduction of (non)metal dopants enables the photocatalysts to absorb visible light (Supplementary Data, Fig. S6).

3. Results and discussion

3.1. Effect of background effluent matrix on photocatalytic pharmaceutical degradation

To explore the dependence of the photocatalytic treatment efficacy on the wastewater effluent characteristics, the kinetic rates for TiO₂-mediated photocatalytic degradation of acetaminophen and carbamazepine in SWE samples with different origins were monitored under irradiation of UV-C, UV-A, and fluorescent light (Fig. 1). The scavenging effect was evaluated in aqueous TiO₂ suspensions containing different initial concentrations of the target pharmaceuticals (i.e., 1, 3, and 5 μM). Sorption in the dark and direct photolysis with fluorescent light did not lead to any detectable degradation of the pharmaceuticals (Supplementary Data, Table S1). Whereas insignificant photolytic decomposition occurred under UV-A irradiation (Supplementary Data, Table S1), acetaminophen and carbamazepine were vulnerable to photo-oxidation with UV-C light (Supplementary Data, Fig. S7). Photo-irradiation of aqueous TiO₂ suspensions markedly accelerated the degradation of pharmaceuticals relative to direct UV photolysis alone (e.g., k(acetaminophen) = 0.0032 ± 0.0004 min⁻¹ for UV-A in GJ versus 0.1154 ± 0.0135 min⁻¹ for TiO₂/UV-A in GJ; k(carbamazepine) = 0.0208 ± 0.0006 min⁻¹ for UV-C in JR versus 0.4734 ± 0.0280 min⁻¹ for TiO₂/UV-C in JR), which corroborates the key role of •OH as a non-selective oxidant in TiO₂-mediated photocatalytic oxidation. Regardless of the type of applied light source and initial concentration, the presence of the wastewater effluent matrix kinetically retarded the photocatalytic degradation of pharmaceuticals (Fig. 1), which is compatible with the scavenging behavior of effluent-derived chemical species during the treatment of pharmaceutical micropollutants using H₂O₂/UV [26]. In particular, the photocatalytic experiments using SWE samples with different background water quality parameters suggest an inverse correlation between the pseudo first-order rate constant for pharmaceutical oxidation and concentration of dissolved organic matter or alkalinity (Fig. 1).

To examine the impact of the background constituents on the kinetics for degradation of pharmaceutical compounds,
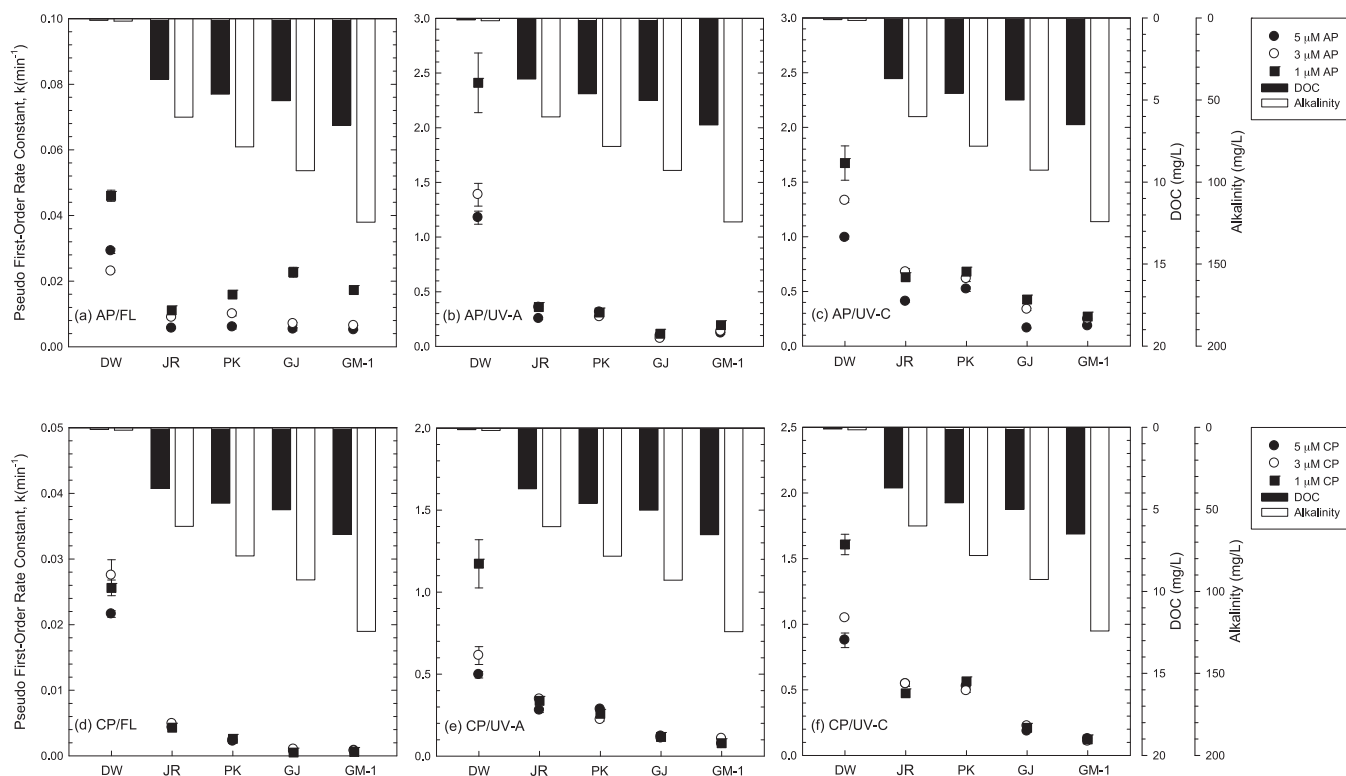
Fig. 1. Effects of variations in the dissolved organic carbon (DOC) and alkalinity on the kinetics for photocatalytic degradation of acetaminophen (AP) and carbamazepine (CP) in distilled water (DW) and secondary wastewater effluents (from Jungrang (JR), Pankyo (PK), Gwangju (GJ), and Gumi (GM-1) wastewater treatment plants) under irradiation of fluorescent (FL), UV-A, and UV-C light ([TiO_2]$_0$ = 0.5 g/L; [acetaminophen]$_0$ = [carbamazepine]$_0$ = 1, 3, and 5 μM; pH$_i$ = 8.0 for distilled water, pH$_i$ was not adjusted for secondary wastewater effluents).

photocatalyzed oxidation of trace levels of carbamazepine was performed with varying bicarbonate alkalinity and initial concentrations of chloride (Cl^-), nitrate (NO_3^-), and humic acid (as a surrogate for dissolved organic matter) (Fig. 2). Although catalyst fouling and the quenching of oxidizing radicals (i.e., •OH and

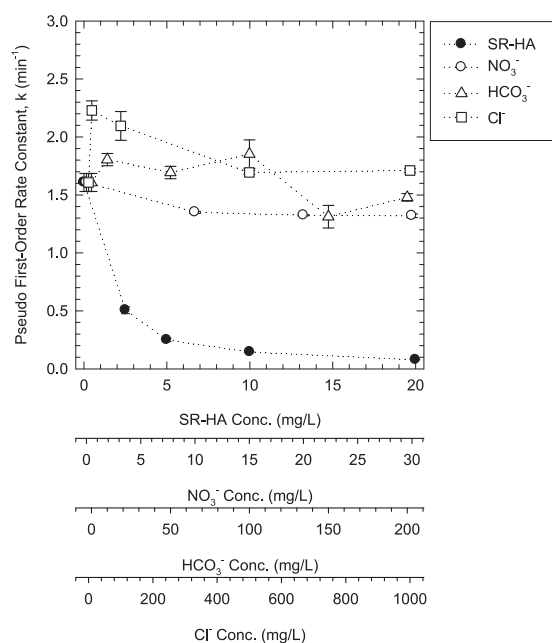**Fig. 2.** Photocatalytic degradation of carbamazepine using the TiO_2/UV-C system as a function of the bicarbonate alkalinity (HCO_3^-) and initial concentration of nitrate (NO_3^-), chloride (Cl^-), and humic acid (SR-HA) ([TiO_2]$_0$ = 0.5 g/L; [carbamazepine]$_0$ = 1 μM; pH$_i$ = 8.0).

valence band (VB) hole) by Cl^- can inhibit TiO_2 photocatalytic activity [27], the typical Cl^- concentrations of the effluent did not affect the oxidation of carbamazepine in the UV-C irradiated aqueous TiO_2 suspensions (Fig. 2). The presence of NO_3^- that causes strong UV absorption of the secondary effluent (Supplementary Data, Fig. S8) possibly hinders photon absorption by water-dispersed TiO_2 as a prerequisite step for photo-generation of electron–hole pairs. On the other hand, based on previous studies reporting a role of NO_3^- as the primary precursor of •OH in surface water [28], it is probable that •OH produced by UV photolysis of NO_3^- contributes to oxidative degradation. Despite the scenarios for potential impacts, the rate of the photocatalytic oxidation of carbamazepine was not notably changed as the initial concentration of NO_3^- increased (Fig. 2).

Autin et al. demonstrated that increased alkalinity results in a significant drop in photocatalytic performance in pollutant degradation due to the formation of TiO_2 aggregates [26], which appears to be compatible with the negative correlation between alkalinity and the photocatalytic activity of TiO_2 for pharmaceutical degradation (Fig. 1). In contrast to the apparent inhibitory effect of alkalinity, the rate of photocatalytic carbamazepine oxidation changed negligibly with increasing bicarbonate concentration (Fig. 2). On the other hand, the kinetics for the photocatalyzed degradation of carbamazepine were inversely related to the initial concentration of humic acid (Fig. 2), which suggests that quenching of •OH by effluent organic matter is primarily responsible for the kinetic retardation of photocatalytic pharmaceutical degradation in secondary effluent matrices. In particular, measurement of the rate constant for photochemical oxidation using H_2O_2/UV as a function of the background constituents confirms that competition for •OH between the target pharmaceutical and dissolved organic matter is critical to the scavenging effect of the wastewater effluent matrix (Supplementary Data, Fig. S9).
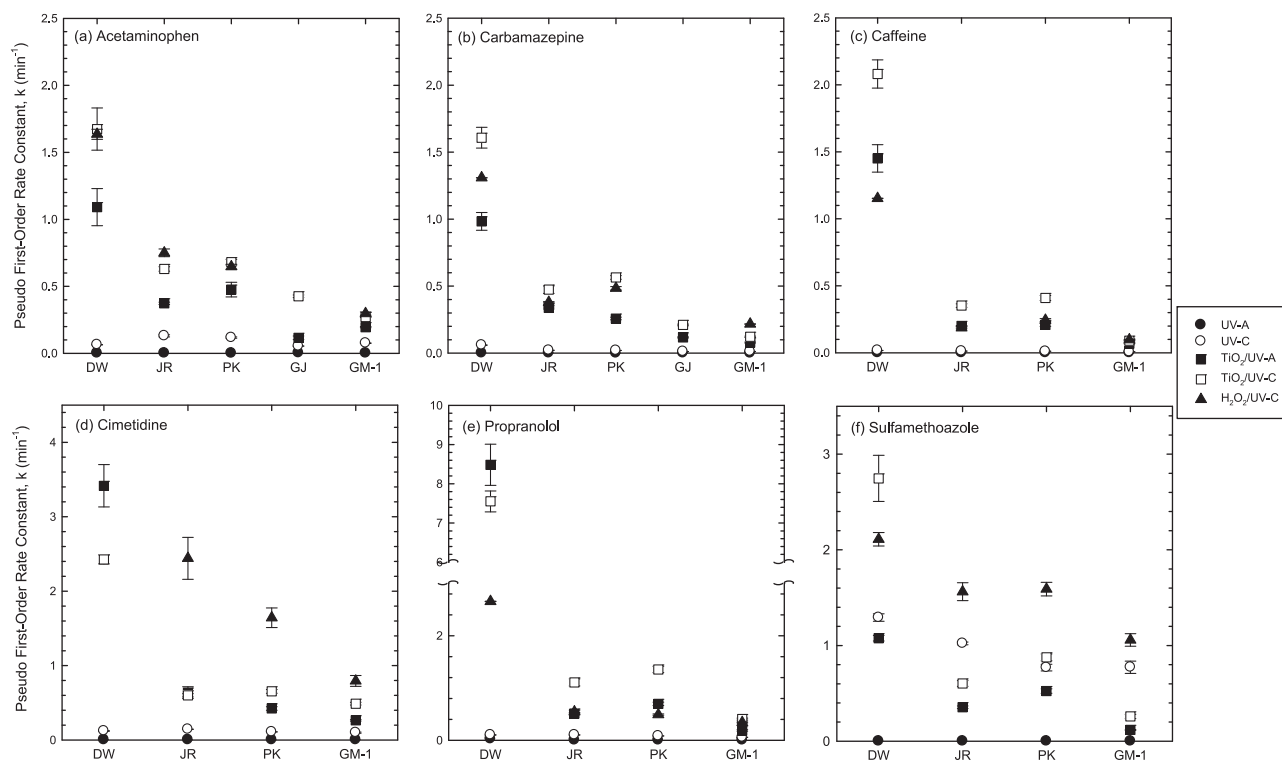
Fig. 3. Comparison of the kinetic rates for the oxidative degradation of pharmaceuticals by UV photolysis and TiO_2/UV-A, TiO_2/UV-C, and H_2O_2/UV-C systems in distilled water (DW) and secondary wastewater effluents (from Jungrang (JR), Pankyo (PK), Gwangju (GJ), and Gumi (GM-1) wastewater treatment plants) ($[TiO_2]_0 = 0.5$ g/L; $[H_2O_2]_0 = 5$ mg/L; [target pharmaceuticals]$_0 = 1$ μM; $pH_i = 8.0$ for distilled water, pH_i was not adjusted for secondary wastewater effluents).
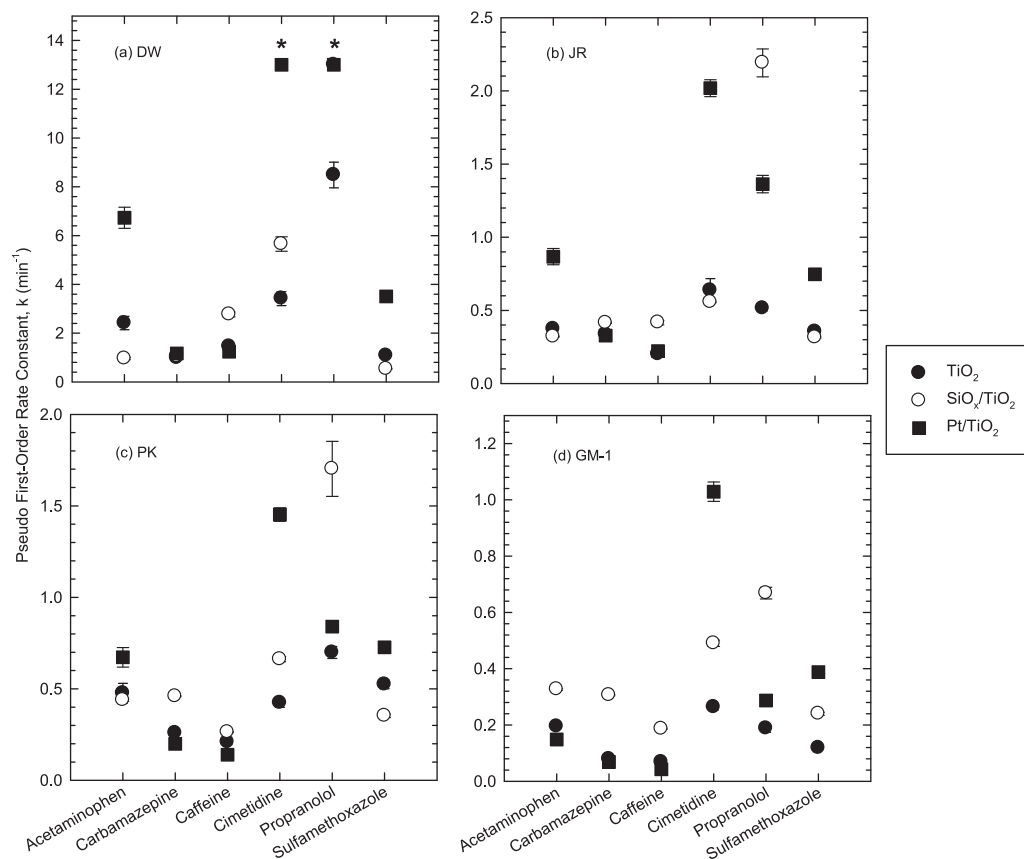

Fig. 4. Pseudo first-order rate constants for the photocatalytic oxidation of pharmaceuticals using TiO_2/UV-A, SiO_x/TiO_2/UV-A, and Pt/TiO_2/UV-A systems in distilled water (DW) and secondary wastewater effluents (from Jungrang (JR), Pankyo (PK), and Gumi (GM-1) wastewater treatment plants) as a function of the target substrate ($[TiO_2]_0 = [SiO_x/TiO_2]_0 = [Pt/TiO_2]_0 = 0.5$ g/L; [target pharmaceutical]$_0 = 1$ μM; $pH_i = 8.0$ for distilled water, pH_i was not adjusted for secondary wastewater effluents). "*" indicates complete degradation within 5 s.
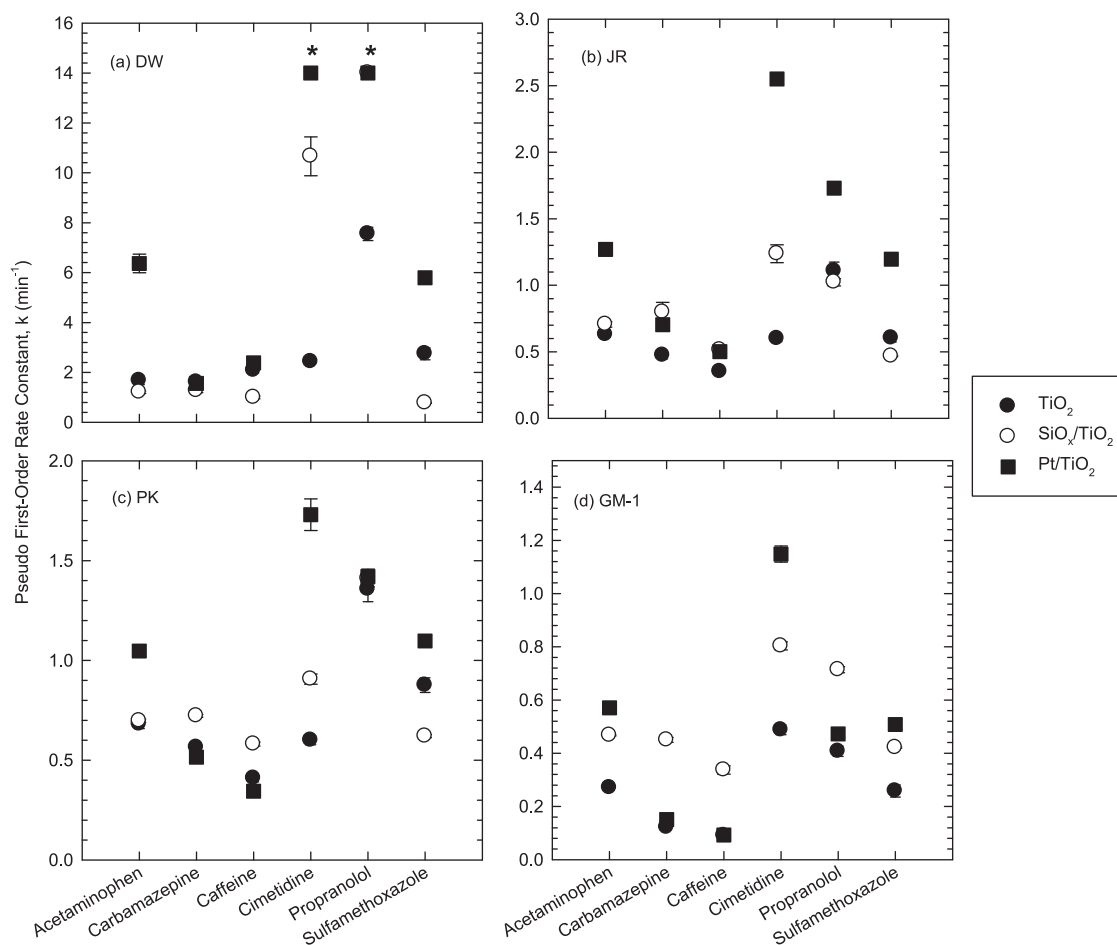
Fig. 5. Pseudo first-order rate constants for the photocatalytic oxidation of pharmaceuticals using TiO_2/UV-C, SiO_x/TiO_2/UV-C, and Pt/TiO_2/UV-C systems in distilled water (DW) and secondary wastewater effluents (from Jungrang (JR), Pankyo (PK), and Gumi (GM-1) wastewater treatment plants) as a function of the target substrate ($[TiO_2]_0 = [SiO_x/TiO_2]_0 = [Pt/TiO_2]_0 = 0.5$ g/L; [target pharmaceutical]$_0 = 1$ μM; $pH_i = 8.0$ for distilled water, pH_i was not adjusted for secondary wastewater effluents). "*" indicates complete degradation within 5 s.

3.2. Photocatalytic oxidation of various pharmaceuticals in secondary wastewater effluents

Fig. 3 shows the pseudo first-order rate constants for the photocatalytic degradation of diverse pharmaceutical micropollutants, including acetaminophen, carbamazepine, caffeine, cimetidine, propranolol, and sulfamethoxazole, in SWEs under UV-A and UV-C irradiation. Direct UV-C photolysis and combined H_2O_2/UV-C (with 5 mg/L H_2O_2, which is typical for tertiary treatment) were used for comparison of the extent of performance reduction in the presence of effluent water matrices. Sorption on TiO_2 under dark conditions negligibly reduced the concentrations of all target pharmaceuticals (data not shown). The •OH generating systems, which include TiO_2/UV-A, TiO_2/UV-C, and H_2O_2/UV-C, degraded most of the pharmaceuticals at a substantially faster rate than UV-C photolysis alone (Fig. 3). In contrast, photoliable sulfamethoxazole was more vulnerable to direct UV-C irradiation than to oxidation with •OH produced from photoirradiated TiO_2 suspensions, which suggests that TiO_2-based photocatalytic treatment may not be suitable for the removal of pharmaceuticals with a high quantum yield for photolytic decomposition (Fig. 3f).

Despite their strong UV absorption capacity (Supplementary Data, Fig. S8), effluent water constituents negligibly affected the rate of photolytic pharmaceutical degradation. On the other hand, the efficiencies of TiO_2/UV-A, TiO_2/UV-C, and H_2O_2/UV-C systems

for the treatment of a broad spectrum of target pharmaceuticals in the presence of different effluent compositions are inversely dependent on the concentration of dissolved organic carbon (Fig. 3), which confirms that the •OH quenching capacity of effluent organic matter is a crucial determinant of the scavenging activity of the effluent matrix. In particular, heterogeneous systems (i.e., TiO_2/UV-A and TiO_2/UV-C) showed more significant retardation of the rate of pharmaceutical degradation in secondary effluent as a background solution than the homogeneous system (i.e., H_2O_2/UV-C): The ratio of the pseudo first-order rate constant for pharmaceutical oxidation in secondary effluent (DW) to that for pharmaceutical oxidation in distilled water (SE), i.e., k_D/k_{SE}, for propranolol is 16.53 (k_D/k_{JR}) using TiO_2/UV-A versus 4.89 using H_2O_2/UV-C and for sulfamethoxazole is 10.64 (k_D/k_{GM}) for TiO_2/UV-C versus 1.99 for H_2O_2/UV-C. The higher susceptibility of the photocatalytic performance to variation in the organic matter concentration is compatible with the observation that the degradation efficiency of TiO_2/UV-C dropped more significantly with increasing concentration of humic acid than that of H_2O_2/UV-C (Fig. 2 and Fig. S9). The further reduction in activity may imply that effluent organic constituents hinder the photocatalytic treatment of micropollutants in two ways: (1) by providing a substantial quantity of organic moieties to scavenge photogenerated •OH and (2) by absorbing onto TiO_2, which reduces the availability of surface active sites for the target substrate, and undergoing oxidation with surface-bound •OH.
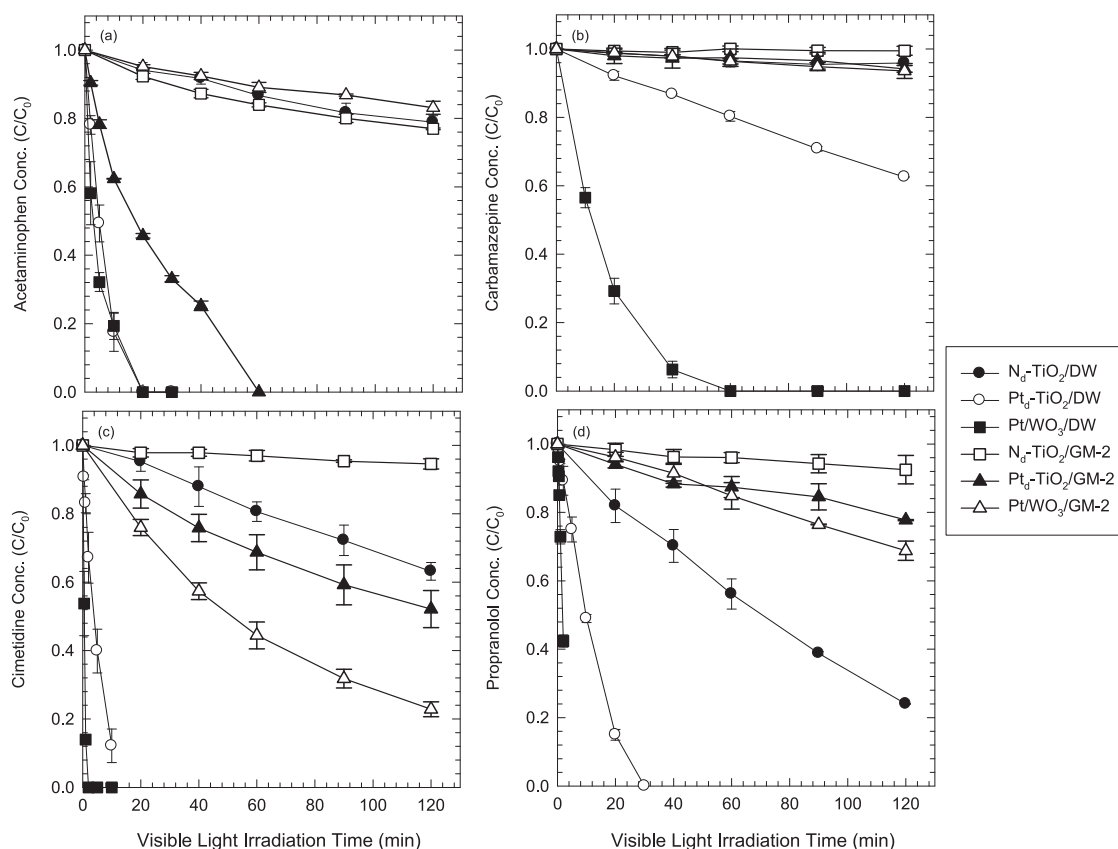
Fig. 6. Photocatalytic degradation of pharmaceuticals by visible light active photocatalysts (i.e., N_d-TiO_2, Pt_d-TiO_2, and Pt/WO_3) in distilled water (DW) and GM-2 secondary wastewater effluent under irradiation ($\lambda > 400\,nm$) ([N_d-TiO_2]$_0$ = [Pt_d-TiO_2]$_0$ = [Pt/WO_3]$_0$ = 0.5 g/L; [target pharmaceutical]$_0$ = 1 μM; pH$_i$ = 8.0 for distilled water, pH$_i$ was not adjusted for secondary wastewater effluent).

3.3. Effect of TiO$_2$ surface modifications

The activities of pure and surface-modified TiO_2 (i.e., SiO_x/TiO_2 and Pt/TiO_2) photocatalysts were compared based on their efficiencies for the removal of pharmaceutical micropollutants in JR secondary wastewater effluent (Supplementary Data, Fig. S10). Loading the catalysts with silicon oxides enhances the sorption capacity toward organic compounds and makes the surface charge of the catalyst predominantly negative at pH > 2 [17]. Nano-sized platinum deposits on the TiO_2 surface function as electron sinks to inhibit the recombination of photogenerated electron–hole pairs, thereby increasing the efficiency of the production of •OH [23,29]. Oxidizing capacity of surface-modified TiO_2 relative to pure TiO_2 was evaluated based on the kinetic rates of photocatalytic oxidation of benzoic acid and methanol as probe compounds for •OH yield (Supplementary Data, Fig. S11). The photocatalytic activity for oxidative conversion of benzoic acid (or methanol) to p-hydroxybenzoic acid (or formaldehyde) was found to be in the order of Pt/TiO_2 > TiO_2 ≫ SiO_x/TiO_2, which assures that surface loading of platinum facilitates charge separation in TiO_2 to result in the enhanced production of •OH.

The overall improvement of the photocatalytic activity through TiO_2 surface modification was confirmed by the kinetic enhancement of the treatment of pharmaceuticals in UV-C irradiated JR secondary effluent containing SiO_x/TiO_2 or Pt/TiO_2 (Supplementary Data, Fig. S10). In particular, modified TiO_2 under UV-A irradiation degraded selected pharmaceuticals faster than pure TiO_2 under UV-C irradiation: The removal efficiency (R) of caffeine was 49.25 ± 0.07% using TiO_2/UV-C versus 59.85 ± 6.58% using SiO_x/TiO_2/UV-A, while that of sulfamethoxazole was 63.25 ± 7.42% using TiO_2/UV-C versus 76.25 ± 1.90% using Pt/TiO_2/UV-A. The

improved activity of Pt/TiO_2 for photocatalyzed degradation of pharmaceuticals correlates well with the accelerated oxidative conversion of methanol and benzoic acid as indirect indication for •OH generation. On the other hand, the increased efficiency of SiO_x/TiO_2 for pharmaceutical removal seems to be somewhat incompatible with the low quantum yield for photoproduction of •OH. Such an empirical inconsistency implies that kinetic enhancement in degradation of micropollutants over photo-irradiated SiO_x/TiO_2 is primarily attributed to the superior surface affinity toward organic substances. In that photocatalytic performance assessment using chemical indicators is proper to measure •OH in homogeneous reaction media, there is a need for further study to identify the contribution of surface-bound oxidants to heterogeneous photocatalytic degradation by SiO_x/TiO_2.

Photolytic experiments using surface-modified TiO_2 for the treatment of diverse pharmaceuticals in secondary effluents confirm that the rate of photocatalytic degradation is inversely related to the concentration of effluent organic matter (Supplementary Data, Figs. S12 and S13). Considering that the efficiency of heterogeneous photocatalytic reactions is highly dependent on the affinity of the reactant for the catalyst surface, TiO_2 surface modifications may cause preferential degradation of specific organic pollutants. The results shown in Figs. 4 and 5 suggest that the extent of the enhancement of photocatalysis by modification of the TiO_2 surface depends on the target pharmaceutical. For instance, surface platinization significantly favors the photocatalytic degradation of acetaminophen and cimetidine, as is evident from the marked kinetic acceleration: The k_D for acetaminophen is 2.4101 ± 0.2734 min^{-1} using TiO_2/UV-A versus 6.7308 ± 0.4313 min^{-1} using Pt/TiO_2/UV-A and the k_{JR} for cimetidine is 0.5995 ± 0.0223 min^{-1} using TiO_2/UV-C

versus $2.5509 \pm 0.0427\,min^{-1}$ using $Pt/TiO_2/UV$-C. The increase in the photocatalytic activity of SiO_x/TiO_2 was more noticeable for the oxidative degradation of propranolol: The k_{JR} for propranolol is $0.5131 \pm 0.0179\,min^{-1}$ using TiO_2/UV-A versus $2.1911 \pm 0.0954\,min^{-1}$ using $SiO_x/TiO_2/UV$-A. In contrast, the treatability ratings of pharmaceuticals were relatively invariant with changing background water composition within the range investigated, although the electrostatic interactions between the catalyst surface and constituents in secondary effluent involve altering the surface charge of pure or modified TiO_2 (Supplementary Data, Fig. S14).

3.4. Application of visible-light-active photocatalysts

Visible-light-responsive photocatalysts, including N_d-TiO_2, Pt_d-TiO_2, and Pt/WO_3, were applied to the oxidative degradation of pharmaceutical micropollutants in distilled water and GM secondary effluent (GM-2) under irradiation ($\lambda > 400\,nm$) (Fig. 6). All target pharmaceuticals were effectively oxidized with Pt/WO_3, on which visible light induced the generation of conduction band (CB) electrons leading to sequential reduction of O_2 to $^\bullet OH$ [30,31]. On the other hand, the photocatalytic activity of doped TiO_2 for pollutant oxidation is substrate specific due to the selective nature of the photogenerated VB hole (i.e., it is unable to oxidize water or hydroxide ions to $^\bullet OH$) [32,33]; therefore, the photocatalytic degradation of carbamazepine by Pt_d-TiO_2 proceeded at a much slower rate than that of other pharmaceuticals, and cimetidine and propranolol were preferably degraded in photoirradiated suspensions of N_d-TiO_2 (Fig. 6). Similar to pure and surface-modified TiO_2, the pharmaceutical oxidation performance of visible-light-active photocatalysts is drastically reduced in the presence of a background water matrix, which implies effective quenching of the photogenerated VB holes (as well as $^\bullet OH$) in the secondary effluent. Comparison of the kinetic rates of the visible-light-induced degradation of pharmaceuticals in distilled water and wastewater effluent reveals that the photocatalytic activity of Pt/WO_3 was much more significantly decreased by the presence of background organic constituents than that of Pt_d-TiO_2 (k_D/k_{GM} (acetaminophen) = 113 using Pt/WO_3 versus 4.63 using Pt_d-TiO_2; k_D/k_{GM} (carbamazepine) = 113.33 using Pt/WO_3 versus 7.6 using Pt_d-TiO_2; k_D/k_{GM} (cimetidine) = 143.72 using Pt/WO_3 versus 35.98 using Pt_d-TiO_2; k_D/k_{GM} (propranolol) = 127.23 using Pt/WO_3 versus 42.14 using Pt_d-TiO_2). The result implies that substrate-dependent activity of the primary oxidant (i.e., VB hole) allows efficient treatment of a selected group of micropollutants by doped TiO_2 in the presence of background matrix; this is in contrast to non-selective $^\bullet OH$-mediated oxidation, which continues to be hindered until complete mineralization of effluent organic matter as $^\bullet OH$ scavenger.

4. Conclusions

This study focused on the impact of background constituents and catalyst modifications on the heterogeneous photocatalytic treatment of pharmaceutical micropollutants. Photolytic experiments using effluents with varying water quality identified dissolved organic matter as a critical constituent for quenching photocatalytic oxidation in SWE; this was confirmed by the inverse correlation between the degradation rate and concentration of humic acid, which is a proxy for the effluent organic matter. Comparison of the rates of pharmaceutical degradation using TiO_2/UV-A, TiO_2/UV-C, and H_2O_2/UV-C systems demonstrated that the photocatalytic performance of the TiO_2-based catalysts decreased more significantly with increasing concentration of dissolved organic carbon; this is likely due to competition

between the target pharmaceutical and effluent organic matter for the surface active sites of TiO_2 and photogenerated $^\bullet OH$. A similar scavenging behavior of the secondary effluent matrix was observed during photocatalytic degradation using various modified photocatalysts, including Pt/TiO_2, SiO_x/TiO_2, N_d-TiO_2, Pt_d-TiO_2, and Pt/WO_3. Catalyst modifications could improve photocatalytic performance in terms of surface affinity, efficiency for $^\bullet OH$ production, and visible light sensitivity. The $Pt/TiO_2/UV$-A and $SiO_x/TiO_2/UV$-A systems outperformed the TiO_2/UV-C system for the treatment of selected pharmaceuticals, and Pt_d-TiO_2 and Pt/WO_3 caused faster degradation with visible light than TiO_2 with fluorescent light, which suggests potential applications in low-energy-demanding photocatalytic processes. Based on their favorable interactions with specific organic moieties and the selective reactivity of photogenerated oxidants, photocatalytic systems that use TiO_2 surface-deposited or doped with (non)metal elements potentially enable preferential removal of high priority micropollutants in complicated water matrices.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2013.08.032.

References

[1] M.M. Huber, S. Canonica, G.Y. Park, U. Von Gunten, Environ. Sci. Technol. 37 (2003) 1016–1024.
[2] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671–698.
[3] J.J. Pignatello, E. Oliveros, A. MacKay, Crit. Rev. Environ. Sci. Technol 36 (2006) 1–84.
[4] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513–886.
[5] J. Kiwi, C. Pulgarin, P. Peringer, Appl. Catal. B Environ. 3 (1994) 335–350.
[6] J.H. Suh, M. Mohseni, Water Res. 38 (2004) 2596–2604.
[7] S. Carbonaro, M.N. Sugihara, T.J. Strathmann, Appl. Catal. B Environ. 129 (2013) 1–12.
[8] I. Kim, N. Yamashita, H. Tanaka, J. Hazard. Mater. 166 (2009) 1134–1140.
[9] B. Halling-Sorensen, S.N. Nielsen, P.F. Lanzky, F. Ingerslev, H.C.H. Lutzhoft, S.E. Jorgensen, Chemosphere 36 (1998) 357–394.
[10] M.D. Hernando, M. Mezcua, A.R. Fernandez-Alba, D. Barcelo, Talanta 69 (2006) 334–342.
[11] A. Joss, S. Zabczynski, A. Gobel, B. Hoffmann, D. Loffler, C.S. McArdell, T.A. Ternes, A. Thomsen, H. Siegrist, Water Res. 40 (2006) 1686–1696.
[12] J. Radjenovic, M. Petrovic, F. Ventura, D. Barcelo, Water Res. 42 (2008) 3601–3610.
[13] M.C. Dodd, H.P.E. Kohler, U. Von Gunten, Environ. Sci. Technol. 43 (2009) 2498–2504.
[14] W. Li, V. Nanaboina, Q.X. Zhou, G.V. Korshin, Water Res. 46 (2012) 403–412.
[15] R. Rosal, A. Rodriguez, J.A. Perdigon-Melon, M. Mezcua, M.D. Hernando, P. Leton, E. Garcia-Calvo, A. Aguera, A.R. Fernandez-Alba, Water Res. 42 (2008) 3719–3728.
[16] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69–96.
[17] J. Lee, W.Y. Choi, J. Yoon, Environ. Sci. Technol. 39 (2005) 6800–6807.
[18] K. Ikehata, N.J. Naghashkar, M.G. Ei-Din, Ozone Sci. Eng. 28 (2006) 353–414.
[19] M. Klavarioti, D. Mantzavinos, D. Kassinos, Environ. Int. 35 (2009) 402–417.
[20] N. De la Cruz, R.F. Dantas, J. Gimenez, S. Esplugas, Appl. Catal. B Environ. 130 (2013) 249–256.
[21] V.A. Sakkas, P. Calza, C. Medana, A.E. Villioti, C. Baiocchi, E. Pelizzetti, T. Albanis, Appl. Catal. B Environ. 77 (2007) 135–144.
[22] L. Yang, L.E. Yu, M.B. Ray, Water Res. 42 (2008) 3480–3488.
[23] J.S. Lee, W.Y. Choi, Environ. Sci. Technol. 38 (2004) 4026–4033.
[24] J. Ryu, S. Kim, Mater. Trans. 53 (2012) 2200–2204.
[25] Y. Wang, C.X. Feng, M. Zhang, J.J. Yang, Z.J. Zhang, Appl. Catal. B Environ. 100 (2010) 84–90.

[26] O. Autin, J. Hart, P. Jarvis, J. MacAdam, S.A. Parsons, B. Jefferson, Water Res. 47 (2013) 2041–2049.
[27] A. Piscopo, D. Robert, J.V. Weber, Appl. Catal. B Environ. 35 (2001) 117–124.
[28] R.G. Zepp, J. Hoigne, H. Bader, Environ. Sci. Technol. 21 (1987) 443–450.
[29] J.S. Lee, W.Y. Choi, J. Phys. Chem. B 109 (2005) 7399–7406.
[30] J. Kim, C.W. Lee, W. Choi, Environ. Sci. Technol. 44 (2010) 6849–6854.
[31] H. Lee, J. Choi, S. Lee, S.-T. Yun, C. Lee, J. Lee, Appl. Catal. B Environ. 138–139 (2013) 311–317.
[32] S. Kim, S.J. Hwang, W.Y. Choi, J. Phys. Chem. B 109 (2005) 24260–24267.
[33] M. Mrowetz, W. Balcerski, A.J. Colussi, M.R. Hoffmann, J. Phys. Chem. B 108 (2004) 17269–17273.